Theoretical study of the intrinsic magnetic properties of disordered $Fe_{1-x}Ru_x$ alloys: a mean-field approach

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(Dated: March 25, 2008)

Abstract

The magnetic properties of the $Fe_{1-x}Ru_x$ alloy system for $0 \leq x \leq 0.10$ are studied by using a mean-field approximation based on the Bogoliubov inequality. Ferromagnetic Fe-Fe spin correlations and antiferromagnetic Fe-Ru and Ru-Ru exchanges have been considered to describe the temperature dependence of the Curie temperature and low temperature magnetization. A composition dependence has been imposed in the exchange couplings, as indicated by experiments. From a least-square fitting procedure to the experimental results an estimation of the interaction parameters was obtained, which yielded the low temperature dependence of the magnetization and of the ferromagnetic Curie temperature. A good agreement was obtained with available experimental results.

PACS numbers: 75.50.Bb;75.10.Hk;75.10.Nr;75.10.-b

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I. INTRODUCTION

The Fe-based alloys with the 4d transition metals have been intensively investigated since the earliest studies on magnetic materials. Nevertheless, theoretical and experimental results on Fe-Ru systems are scarce [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11]. Iron and ruthenium are miscible over the entire range of composition. The iron-rich Fe-Ru alloys are ferromagnetic (FM) at room temperature in the bcc structure[12]; the Curie temperature decreases steadily with the Ru content. According to recent investigations in disordered $Fe_{1-x}Ru_x$ alloys, for $x < 0.30$ a single phase is formed with a bcc structure, whereas for $x \geq 0.30$ there is a crystallographic transition to an hcp structure [13]. In the bcc phase the lattice parameter has a linear increase with the increase of the Ru concentration. The experimental results evidenced that antiferromagnetic (AF) Fe-Ru exchanges are settled up in dilute alloys which depends on the solute concentration.

First-principles electronic structure calculations on the magnetic phases of iron compounds in the $CsCl$ structure with 4d elements have shown that $FeRu$ indeed has an AF ground state [2]. The introduction of Ru in the immediate neighborhood has been found to enhance the magnetic moment at Fe sites [6]. Actually, a competition mechanism between FM and AF exchanges is expected to occur in Fe-rich $Fe_{1-x}Ru_x$ alloys, although the FM $Fe-Fe$ coupling is expected to be overwhelming. Recent first-principles calculations has also confirmed that with the introduction of Ru atoms in the bcc iron matrix the Fe moment changes appreciably and the average moment decreases steadily [14]. The Ru atom as a single impurity in this host carries a small moment of about 0.27 μ_B , which is ferromagnetically coupled to the surrounding Fe atoms. With the increase of the distance between Ru atoms larger moments have been observed for the Fe atoms in dilute alloys. The contact hyperfine field has also been found to be very sensitive to the separation between Ru atoms in the first shell of neighbors, and scales with the magnetization.

In this study we apply a mean-field approximation based on the Bogoliubov inequality to assess the composition dependence of the intrinsic magnetic properties of disordered $Fe_{1-x}Ru_x$ alloys. Since these alloys are formed in the bcc structure, mean-field-like procedures are expected to be a very good approximation to describe their magnetic behavior. Our model assumes that the $Fe-Fe$ interaction is ferromagnetic, while $Ru-Ru$ and $Fe-Ru$ interactions are antiferromagnetic. The sites on the lattice are occupied either by

a Fe atom or a Ru atom, according to the distribution:

$$\mathcal{P}(\epsilon_i) = (1-x)\delta(\epsilon_i - 1) + x\delta(\epsilon_i), \tag{1}$$

where $\epsilon_i = 1(0)$ for $Fe(Ru)$ atoms. The Hamiltonian reads:

$$\mathcal{H} = -\sum_{<i,j>} J_{ij} S_i S_j, \tag{2}$$

where the sum runs over all pairs of nearest-neighbor sites and $S_i = \pm 1$, for all sites i. Since the atoms are randomly distributed in the lattice, the bond between nearest-neighbor S_i and S_j, J_{ij}, takes the values J for $Fe-Fe$ pairs, $-\alpha J$ for $Fe-Ru$ pairs and $-\xi J$ for $Ru-Ru$ pairs, with probabilities $(1-x)^2$, $2x(1-x)$ and x^2, respectively. We took the assumption that both α and ξ parameters are positive. We will show that it is crucial to take into account a dependence of the exchange interaction on the fraction of Ru atoms. Since from experimental results the lattice parameter varies with the Ru concentration, this dependence is thereby expected.

In the next section we outline the adopted formalism by focusing on the new features, and in Section III we present and discuss the results.

II. CALCULATIONAL DETAILS

The Bogoliubov inequality is a useful way to construct a mean-field-like approximation to a Hamiltonian $\mathcal{H}$ which cannot be solved exactly [15]. It reads:

$$F(\mathcal{H}) \leq \phi(\zeta) \equiv [F_0] + [\langle \mathcal{H} - \mathcal{H}_0 \rangle_0], \tag{3}$$

where $\mathcal{H}_0$ is an exactly solvable tentative Hamiltonian, F_0 is the free energy associated with $\mathcal{H}_0$, $\langle \cdots \rangle_0$ represents averages made on the ensemble defined by $\mathcal{H}_0$ and $[\cdots]$ represents the disorder average. This Hamiltonian depends on the variational parameter(s) ζ. The right-hand side of the previous equation is then minimized with respect to this (these) variational parameter(s), in order to get the best approximation, given the tentative Hamiltonian $\mathcal{H}_0$.

For this work we chose $\mathcal{H}_0$ to be a combination of single-site and single-pair Hamiltonians, namely:

$$\mathcal{H}_0 = -\gamma_S \sum_{i=1}^{n_1} S_i - \sum_{\{j,k\}, j\neq k}^{n_2} J_{ij} S_j S_k - \gamma_P \sum_{j=1}^{2n_2} S_j, \tag{4}$$

where the first sum runs over n_1 isolated sites, the second sum runs over n_2 isolated pairs of spins and the last one runs over the $2n_2$ sites in the isolated pairs, with $N = n_1+2n_2$, where N is the total number of sites. The variational parameters are γ_S and γ_P. The configurational average of the interactions J_{ij} will be made with the probability distribution:

$$\begin{aligned}\mathcal{P}(J_{ij}) \;=\; & (1-x)^2\delta(J_{ij}-J) + 2x(1-x)\delta(J_{ij}+\alpha J) \\ & + x^2\delta(J_{ij}+\xi J). \end{aligned} \tag{5}$$

Note that, if the site occupation is subject to the probability distribution given by Eq. (1), the bonds are no longer independently distributed since the presence of a Ru atom at a site forces the eight bonds that emerge from this site to be either $Ru-Ru$ or $Fe-Ru$. This correlation is *not* taken into account in Eq. (5). However, since in our approximation pairs are independent, this correlation is not present at this level and then we can use Eq. (5) to make the configurational averages.

It is easy to show that the free energy associated with the trial Hamiltonian $\mathcal{H}_0$ is given by:

$$F_0 = -kT\ln(Z_S^{N-2n_2}Z_P^{n_2}), \tag{6}$$

where N is the number of sites, k is the Boltzmann constant, T is the temperature, and

$$Z_S = 2\cosh(\gamma_S/kT) \tag{7}$$

and

$$Z_P(J_{ij}) = 2\exp(J_{ij}/kT)\cosh(2\gamma_P/kT) + 2\exp(-J_{ij}/kT). \tag{8}$$

Therefore:

$$[F_0] = \int F_0\mathcal{P}(J_{ij})dJ_{ij}. \tag{9}$$

In the same way we obtain:

$$\begin{aligned}[\langle\mathcal{H}-\mathcal{H}_0\rangle_0] \;=\; & -\left(\frac{Nz}{2}-n_2\right)m^2\int J_{ij}\mathcal{P}(J_{ij})dJ_{ij} + \\ & (N-2n_2)\gamma_S m + 2n_2\gamma_P m, \end{aligned} \tag{10}$$

where m is the magnetization (see next two equations) and $z = 8$ for the bcc lattice. Then $\phi(\zeta)$ is constructed according to Eq. (3).

The magnetization can be obtained from isolated sites or from isolated pairs, respectively:

$$m_S = \left[\frac{1}{\beta}\frac{\partial\ln Z_S}{\partial\gamma_S}\right] = \tanh(\gamma_S/kT) \tag{11}$$

and

$$m_P = \left[\frac{1}{\beta}\frac{\partial \ln Z_P}{\partial \gamma_P}\right] = 2\sinh(2\gamma_P/kT) \times \left\{(1-x)^2\frac{\exp(J/kT)}{Z_P(J)} + x^2\frac{\exp(-\xi J/kT)}{Z_P(-\xi J)} + 2x(1-x)\frac{\exp(-\alpha J/kT)}{Z_P(-\alpha J)}\right\}, \quad (12)$$

where $\beta = 1/kT$.

Minimizing the approximated free energy with respect to γ_S and taking into account the above expressions for the magnetization, we obtain:

$$\gamma_S = \frac{z}{z-1}\gamma_P. \quad (13)$$

We have chosen $n_2 = zN/2$, which is the maximum number of pairs for a lattice of N sites and coordination number z. Also, $\phi(\zeta)$ decreases when n_2 increases and, therefore, the value we chose for n_2 leads to the minimum value physically meaningful for $\phi(\zeta)$. We believe this to lead to the best approximation possible for the true free energy within our procedure.

By imposing that the two expressions for the magnetization, i.e., Eqs. (11) and (12) are equal, expanding them for small γ_S and γ_P, and using Eq. (13), we obtain:

$$\frac{z}{2(z-1)} = \left\{\frac{(1-x)^2}{1+\exp(-2J/kT)} + \frac{2x(1-x)}{1+\exp(2\alpha J/kT)} + \frac{x^2}{1+\exp(2\xi J/kT)}\right\}. \quad (14)$$

This expression with $z = 8$ can be used to obtain the critical temperature for the bcc lattice as a function of x. The experimental values of these critical temperatures were reported in Ref. 13. We have made a best fitting procedure in order to evaluate the parameters α and ξ; details will be given and the results discussed in Section III. Note that, since we have made an expansion for small γ_S and γ_P, the previous expression is valid only near T_c.

We can also evaluate the magnetization, again imposing that $m_S = m_P$ (see Eqs. 11 and 12) and solving it for γ_S with the help of Eq. (13). Therefore the value of γ_S can be used in Eq. (11) to evaluate m_S. See next section for results and discussion.

III. RESULTS AND DISCUSSION

The procedure outlined in the previous section can be used to obtain the value of the exchange constant, J, for pure iron. In this case, the experimental value for the critical temperature is $T_c = 1043\ K$; from Eq. (14) with $x = 0$, we obtain $J = 12.9\ meV$. This value agrees with that one found in Ref. 13 and is within the range $10 - 50\ meV$, as expected for Fe, Co, and Ni [16].

Eq. (14) can also be used to adjust the parameters to fit the experimental values for the critical temperature as function of the Ru fraction, x (see Table I). The experimental values were taken from Ref. 13. To show that it is indeed necessary to take into account a variation of the AF interaction constants with x, we have plotted in Fig. 1 the critical temperatures given by Eq. (14) with $\alpha = \xi = 1.0$ (squares) and $\alpha = \xi = 0.79$ (triangles). This last value is the one which makes the experimental and theoretical values coincide for $x = 0$ and $x = 0.02$. Clearly, a constant AF interaction will not adjust the experimental values. We then propose a concentration dependence for the AF interactions, as has been pointed out in Ref. 13. Since we have only five experimental values of T_C for the disordered alloy, we will assume that (see Eq. (5)):

$$\alpha \equiv \xi = \alpha_0 - \alpha_1\, x. \tag{15}$$

The values we obtain with a non-linear least-square-fitting method are:

$$\alpha_0 = 0.54(2); \quad \alpha_1 = 5.4(4), \tag{16}$$

where the values in parentheses are the errors in the last decimal figure. In Fig. 1 the theoretical curve is represented by a dashed line, while the experimental results are represented by open circles (error bars are smaller than the points). As it can be seen, the agreement between the adjusted curve and the experimental is excellent.

We have also calculated the magnetization for some values of x, as outlined at the end of the previous section. The results are depicted in Fig. 2: as expected, the critical temperature decreases as the concentration of Ru is increased. Since we have used a mean-field approximation, static critical exponents assume their classical values. Therefore, the question of universality classes cannot be addressed by the present procedure. We are now performing a Monte Carlo simulation on this alloy to calculate thermodynamic quantities

and some critical exponents. Note the inset in Fig. 2: we expect that the zero-temperature value of the magnetization varies with x, since the introduction of AF interactions will freeze some of the spins in the reversed position, when compared to the Fe background. In fact, $m(T=0)$ decreases as the fraction of Ru is increased, as noted for $x = 0.02, 0.04$ and 0.06. For $x = 0.10$ the AF bonds are no more present: for the values of the adjusted parameters α_0 and α_1 (see Eqs. (15) and (16)) and for $x = 0.10$, $\alpha = \xi = 0$ and the Ru atoms act as nonmagnetic impurities. Since the fraction of magnetic (Fe) atoms for $x = 0.10$ is well above the percolation threshold for the bcc lattice, we expect that nearly all Fe atoms take part in the infinite cluster; therefore, the value of the magnetization at $T = 0$, for $x = 0.10$, should be close to 1. As the temperature is raised from zero, the AF bonds (which are weaker than the FM ones) disorder for small values of T and the magnetization increases. Nevertheless, for finite (but still low) temperatures, the behavior of the magnetization is not monotonic with respect to x. This result is a consequence of the balance between two effects: as x increases, m decreases due to a greater number of AF bonds but increases due to the weakening of these bonds. This feature explains the behavior seen in the inset of Fig. 2. The fact that the magnetization returns to 1 as the temperature is increased, for $x = 0.02, 0.04$ and 0.06, may be an artifact of the mean-field approximation: this aspect will be clarified by the Monte Carlo simulation.

In summary, we have calculated the interaction constants for the $Fe_{1-x}Ru_x$ system by using a mean-field approximation based on the Bogoliubov inequality. The agreement between our theoretical predictions and the results of experiments is excellent and shows that it is necessary to take into account a concentration dependence of the antiferromagnetic interac-

TABLE I: Critical temperatures for $Fe_{1-x}Ru_x$; figures in parenthesis are the errors and apply to the last figure (values taken from Ref. 13).

x	T_c
0.0	1043
0.02	968(2)
0.04	928(2)
0.06	908(2)
0.10	838(2)

tion strength. We have also calculated the magnetization as a function of the temperature for some x values, and discussed in detail the expected low temperature behavior. At $T = 0$ the magnetization m decreases as the Ru content x increases for $0 \leq x < 0.10$ but attains the value 1.0 for $x = 0$ and 0.10 . At low but still finite temperatures the dependence of m on x is nonmonotonic, owing to a competition mechanism which arises from the effects introduced as Ru atoms substitutes for Fe: the appearance of antiferromagnetic interactions and their weakening due to the dependence of the antiferromagnetic constant exchange on x. We are now doing a Monte Carlo simulation on this system to calculate thermodynamic quantities and critical exponents.

Acknowledgments

The authors would like to thank the Brazilian Agencies FAPESC, CNPq, and CAPES for partial financial support and I. J. L. Diaz and T. P. de Oliveira for a critical reading of the manuscript.

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FIG. 1: Critical temperature as a function of the Ru concentration. Experimental points are represented by circles. Squares (triangles) represent constant AF interactions, J_{AF}, with $J_{AF}/J = 1.0(0.79)$, where J is the ferromagnetic interaction strength between Fe atoms. The dashed line represents results from a least-square fitting by taking into account that J_{AF} varies with x in the form $J_{AF} = 0.54 - 5.4\,x$.

FIG. 2: Magnetization versus temperature for five different x values. The inset shows details of the magnetization behavior at low temperatures. The legends are the same for both graphs; the outermost curve corresponds to $x = 0$ while the innermost is for $x = 0.10$.